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# First identification of cryptotephra from the Kamchatka Peninsula in a Greenland ice core: Implications of a widespread marker deposit that links Greenland to the Pacific northwest

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## ABSTRACT

Contiguous sampling of Holocene ice from the NGRIP core, Greenland, has revealed a new rhyolitic cryptotephra that is geochemically identical to the KHG tephra, a widespread marker deposit originating from the Khangar volcano, Kamchatka. This is the first identification of tephra from the Kamchatka Peninsula in Greenland ice and the first finding of the KHG tephra outside Kamchatka. The NGRIP KHG has an age of  $7872 \pm 50$  a BP 1950, and this date will help improve age models for Kamchatka, where existing age estimates of KHG are too young, thus highlighting the importance of locating long-range, low-concentration cryptotephra deposits in well-dated ice cores. In Greenland KHG is located close to the termination of the 8.2 ka BP cooling event that is also a climate feature in palaeo-records of Kamchatka. This tie-point therefore provides a unique opportunity to synchronise records of environmental change in distal locations.

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## 1. Introduction

Tephrochronology uses volcanic ash with unique geochemical fingerprints to precisely correlate a diverse range of marine and terrestrial palaeoarchives (e.g. Lowe, 2011). Tephrochronological research has evolved from investigations of visible tephra layers to studies of *cryptotephra* – low concentrations of glass shards, invisible to the naked eye – that still form stratigraphically distinct deposits (e.g. Davies, 2015). Cryptotephra research enormously increases the geographical area where a geochemically characterised tephra layer could serve as a time-synchronous isochron (e.g. Lane et al., 2013; van der Bilt et al., 2017) and ice cores are one of the most important cryptotephra archives, with over 100 layers (predominantly Icelandic origin) found in Greenland records to date (e.g. Mortensen et al., 2005; Davies et al., 2008, 2010; Abbott and Davies, 2012; Coulter et al., 2012; Bourne et al., 2015, 2016).

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The Greenland Ice Core Chronology 2005 (GICC05) was constructed by counting annual layers (of multiple-parameters) in the NGRIP, GRIP and DYE-3 cores down to 42 ka b2k (AD 2000). Correlating both marine and terrestrial tephra layers to those in Greenland is valuable, as a GICC05 age can be transferred to provide chronological control and independently test age models. A detailed Greenland ice core tephrostratigraphy is therefore essential, yet this is lacking for Holocene ice despite the long, well-resolved records (the Holocene in NGRIP is preserved in the top 1492.45 m). The Holocene volcanic event stratigraphy is based predominantly on limited sampling of NGRIP and GISP2 cores for prominent Icelandic eruptions from the last 2000 years (Fiacco et al., 1994; Palais et al., 1991; Zielinski et al., 1995, 1997; Grönvold et al., 1995; Mortensen et al., 2005; Coulter et al., 2012). Although three cryptotephra from North America (Fiacco et al., 1993; Zdanowicz et al., 1999; Jensen et al., 2014) and one from China (Sun et al., 2014) have also been found in Holocene ice. Here we add to the Holocene ice core tephrostratigraphy and report the first ever finding of a cryptotephra from the Kamchatka Peninsula (northwest Pacific) in Greenland and present new major and trace element data from

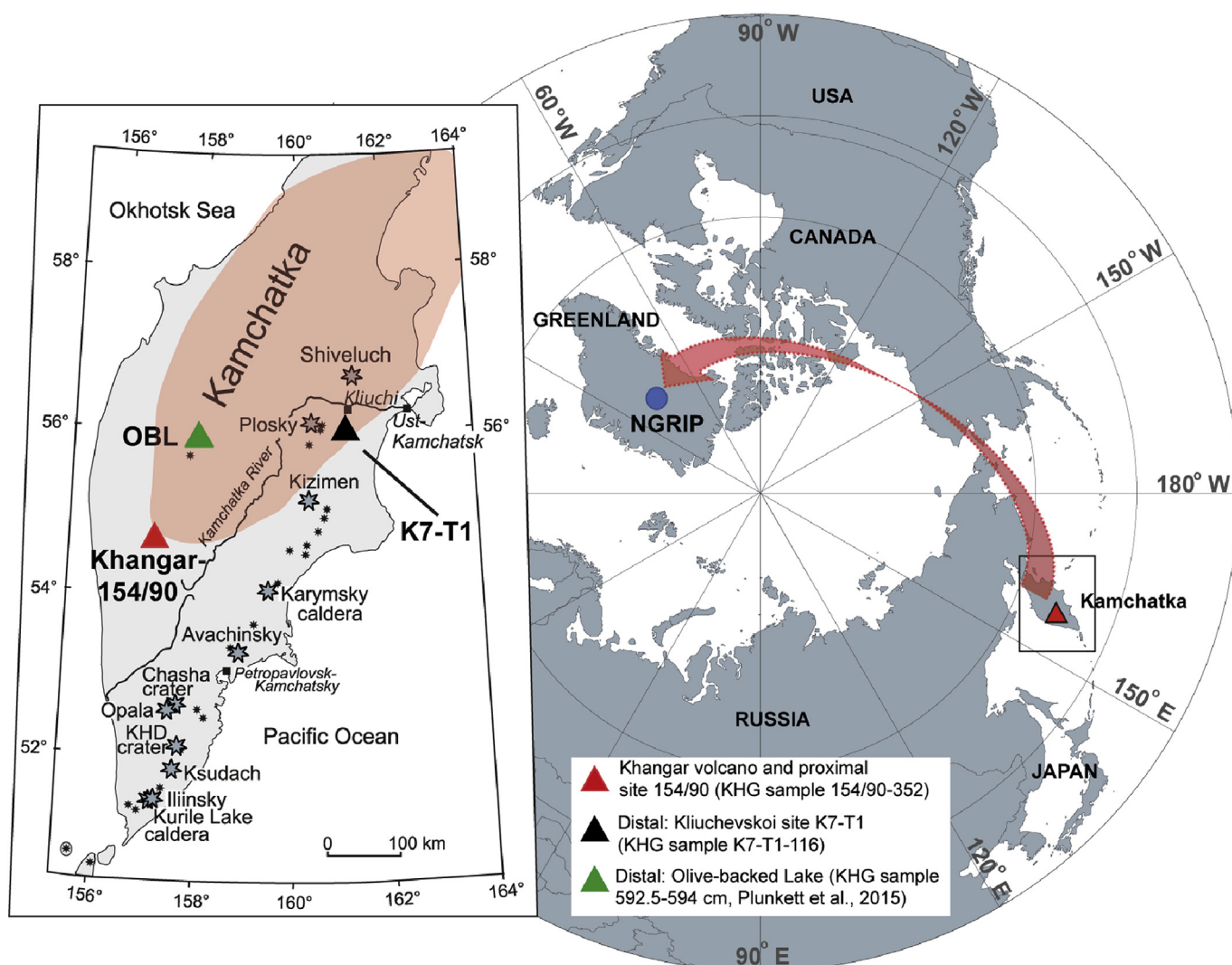
volcanic glass that supports the correlation, in addition to close age estimates. The tephra, named KHG comes from the Khangar volcano (Fig. 1) and is one of the major markers for the Kamchatka Holocene tephrochronological model (Braitseva et al., 1997; Kyle et al., 2011; Plunkett et al., 2015).

## 2. Study locations and methodology

Compositionally unique volcanic glass shards from the KHG eruption were identified as a cryptotephra deposit in the NGRIP ice-core between depths 1199.55 and 1199.40 m as a result of contiguous ice sampling (Table 1; Appendix A). Glass was also extracted from two KHG tephra deposits found in soil sequences on the Kamchatka Peninsula; proximal site 154/90 and distal site K7-T1, 270 km NE of Khangar (Fig. 1; Table 1) and we present new glass geochemistry data for each. NGRIP is located centrally on the Greenland ice sheet, about 5600 km from the Khangar volcano (Fig. 1) and was chosen to investigate Holocene eruption history as it has a robust chronology (GICC05) and datasets for many proxies,

including oxygen isotopes ( $\delta^{18}\text{O}$ ) that were measured at an annual resolution (NGRIP members, 2004; Vinther et al., 2006; Rasmussen et al., 2014). The KHG tephra (labelled KHG<sub>6900</sub> in Plunkett et al., 2015) is a key regional marker deposit (e.g. Braitseva et al., 1997; Kyle et al., 2011; Dirksen et al., 2013), located in the rear of the Kamchatka volcanic arc on the Sredinny Range (Fig. 1) and KHG products include several air-fall and ignimbrite units with a total eruptive volume of 14–16 km<sup>3</sup> (Melekestsev et al., 1996; Braitseva et al., 1997). Ash from this event was dispersed to the northeast and has been traced over 450 km from Khangar (Fig. 1) (Kyle et al., 2011) and deposits have an age range of 7620–7920 cal a BP, based on <sup>14</sup>C dates by Braitseva et al. (1997) and Bazanova and Pevzner (2001) (Table 1). We conducted a geochemical investigation of the NGRIP and KHG terrestrial glass samples by high-precision electron probe microanalysis (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to assess compositional similarity (Table 1).

Ice core sample preparation, instrument set-up and analytical conditions for EPMA and LA-ICP-MS are described in Appendix A,



**Fig. 1.** The location of the NGRIP site in Greenland and the Kamchatka Peninsula, Russia are shown on a circumpolar map of the Northern Hemisphere. A red arrow has been sketched on the map to highlight one possible route for the KHG ash transportation to NGRIP. The inset map (adapted from Kyle et al., 2011) shows the location of the Khangar volcano (red triangle) and three sites containing KHG tephra. Sample 154/90-352 is a visible proximal deposit from the Khangar caldera site 154/90 and sample K7-T1-116 is a visible distal deposit from a terrestrial tephra section. The KHG deposit in Olive-backed lake (OBL) was discovered by Plunkett et al. (2015). The red shading highlights the approximate area of KHG ash fall (Kyle et al., 2011). Large stars show major Holocene explosive centres and small stars show other active volcanoes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 1**

Summary information for the KHG deposits referred to in this study including the GICC05 ice core age (a b2k = AD 2000) and associated maximum counting error (MCE), expressed in years ( $2\sigma$  uncertainty) (Vinther et al., 2006; Rasmussen et al., 2006). The rock type classification (Le Maitre et al., 1989, 2002) and shard size descriptions are given alongside the number of EPMA and LA-ICP-MS analyses obtained from each deposit and the beam and crater size ( $\mu\text{m}$ ) used for each method. All deposits, with the exception of OBL (italics), were identified and analysed as part of this study. OBL data was published by Plunkett et al. (2015). The age range for terrestrial KHG samples (denoted by \*) combines ages from Braitseva et al. (1997), who estimate the age of the KHG deposit to be  $6957 \pm 30$   $^{14}\text{C}$  a BP (7920–7690 cal a BP: 95%), and Bazanova and Pevzner (2001) who estimate the age of the KHG deposit to be  $6872 \pm 15$   $^{14}\text{C}$  a BP (7795–7620 cal a BP: 95%). Laboratory abbreviations are as follows: Tephra Analysis Unit, University of Edinburgh (E-TAU); GEOMAR, Helmholtz Centre for Ocean Research Kiel (GEOMAR); and Christian-Albrechts-Universität zu Kiel (CAU) for trace elements only (T).

Site	Sample Name	Location	Distance from Khangar	Age	Tephra shards	Glass composition	EPMA analyses	LA-ICP-MS analyses	Lab
NGRIP	1199.55–1199.40 m	Greenland 77°45' N 51°07' W	5600 km	7950 $\pm$ 50 a b2k (7872 $\pm$ 50 a BP)	10–30 $\mu\text{m}$	Rhyolitic	14 (3–5 $\mu\text{m}$ )	7 (15–24 $\mu\text{m}$ )	E-TAU GEOMAR CAU (T)
Khangar caldera	90–352	Kamchatka 54.79°N 157.41°E	3 km	7620–7920 cal a BP*	Coarse sand/lapilli >100 $\mu\text{m}$	Rhyolitic	15 (5 $\mu\text{m}$ )	8 (50 $\mu\text{m}$ )	GEOMAR CAU (T)
Kliuchevskoi section	K7-T1-116	Kamchatka 56.15°N 160.82°E	269 km	7620–7920 cal a BP*	Fine ash >100 $\mu\text{m}$	Rhyolitic	12 (5 $\mu\text{m}$ )	–	GEOMAR
K7-T1									
Olive-backed lake (OBL)	592.5–594 cm	Kamchatka 56°12' N 158°51' E	240 km	7620–7920 cal a BP*	Fine ash	Rhyolitic	9 (5 $\mu\text{m}$ )	–	QUB

and raw EPMA data, trace element concentrations and secondary standard data are provided in Appendix B. Geochemical data from glasses were compared using element–element biplots and correlations were supported by two statistical tests; the similarity coefficient of Borchardt et al. (1972) and statistical distance ( $D^2$ ) method of Perkins et al. (1995, 1998).

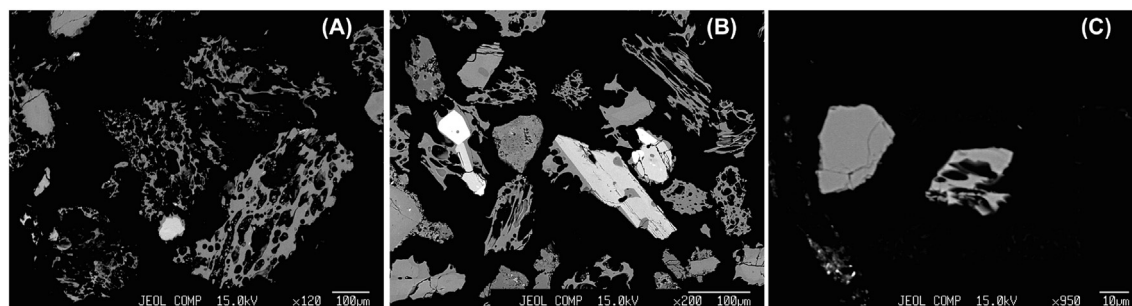
### 3. Chronological and geochemical comparison of the KHG and NGRIP deposits

The KHG cryptotephra is found in NGRIP between 1199.55 and 1199.40 m in Holocene ice and is comprised of 22 colourless/pinkish glass shards with a distinctive bubble-wall morphology, identical in appearance to KHG glass in proximal deposit 154/90–352 and distal deposit K7-T1-116 (Table 1; Fig. 2a–c). The GICC05 age for this deposit is  $7950 \pm 50$  a b2k, or  $7872 \pm 50$  a BP (incorporating a 28-year age correction recommended by Adolphi and Muscheler, 2016) and is located in a warm, stable period (Fig. 3a), approximately 189 years after the end of the 8.2 ka BP cold event (Rasmussen et al., 2014). The ice deposit therefore agrees with KHG  $^{14}\text{C}$  dates of Braitseva et al. (1997) (7920–7690 cal a BP: 95%) in the chronological context. However, radiocarbon ages appear to be too young in general, and specifically, the calibrated age range for KHG from Bazanova and Pevzner (2001) (7795–7620 cal a BP: 95%) does not agree with the GICC05 age. The NGRIP cryptotephra is associated with a significant coeval peak in the electrical conductivity measurement (ECM) profile at 1199.45 m which likely represents the chemostratigraphic signature of the

KHG eruption (Fig. 3b). ECM measures ice acidity ( $\text{H}^+$ ) (e.g. Wolff et al., 1995) and can be used to detect past volcanism, as eruptions produce sulphur-rich gases that are released into the troposphere and stratosphere and are oxidised to produce sulphuric acid ( $\text{H}_2\text{SO}_4$ ).

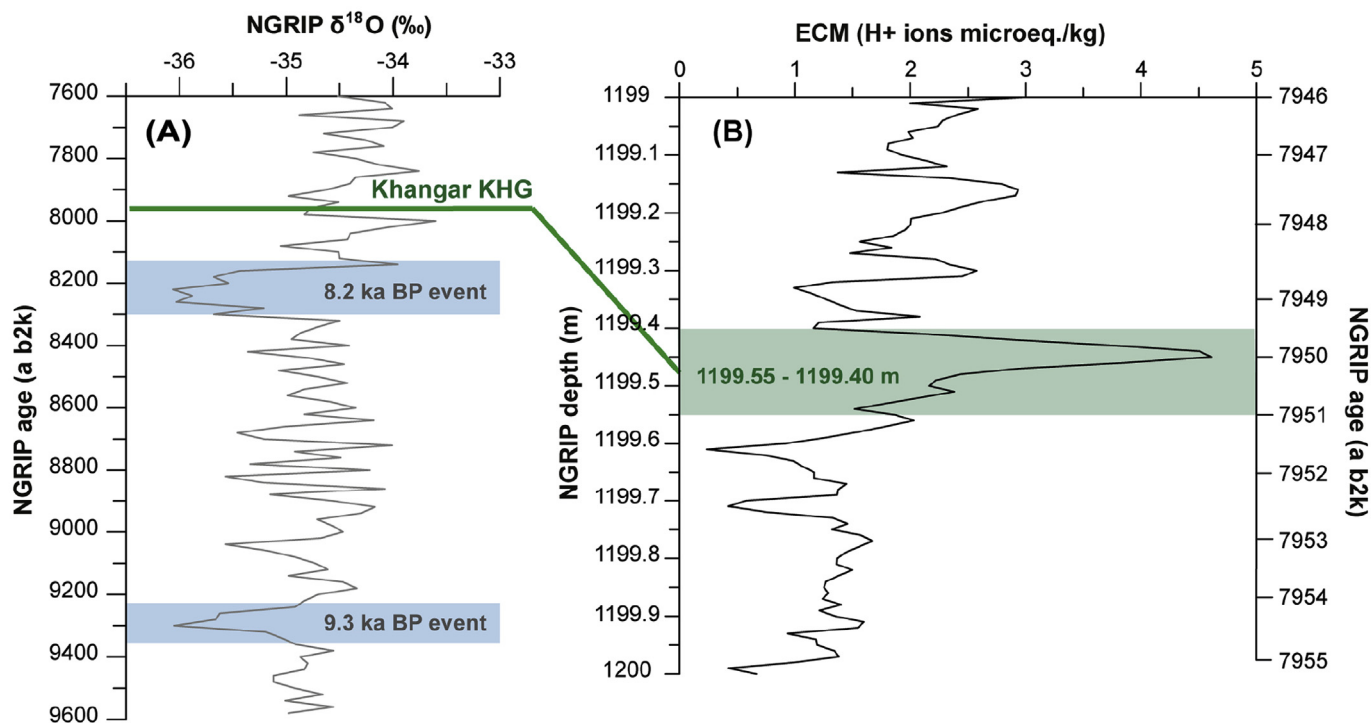
Major element comparison reveals a near identical composition between NGRIP 1199.55–1199.40 m and terrestrial KHG deposits 154/90–352 and K7-T1-116 (Table 2; Appendix B), where all three have a slightly heterogeneous rhyolitic composition with high  $\text{SiO}_2$  content between 74 and 78 % weight (%wt) (Fig. 4a), and a  $\text{K}_2\text{O}$  content ranging between medium and high-K (Fig. 4b) (Le Maitre et al., 1989, 2002). Harker diagrams (Fig. 4a–c) display prominent and well-defined trends, common to all datasets, including increased  $\text{K}_2\text{O}$  with increased  $\text{SiO}_2$  and decreased  $\text{Al}_2\text{O}_3$  with increased  $\text{SiO}_2$ , and cogenetic relationships exist between other elements such as  $\text{CaO}$  and  $\text{FeO}$  (Fig. 4d). The major element composition of our deposits is the same as published KHG data from the Olive-backed Lake (OBL) of central Kamchatka (Fig. 1, Table 1) (Plunkett et al., 2015), also plotted in Fig. 4a–d. Furthermore, statistical analysis of major element sample pairs (Table 3) from NGRIP and individual KHG samples supports a common origin from a single volcanic event, based on high similarity coefficient values of 0.971–0.982 and low  $D^2$  values of 0.404–0.480, below the  $D^2_{\text{critical}}$  value of 18.48 at the 99% confidence level.

Single shards from NGRIP 1199.55–1199.40 m and proximal sample 154/90–352 were analysed by LA-ICP-MS (Table 4) and when average spectra from both are displayed together, there is covariance (Fig. 4e). The mantle-normalised spectra are generally



**Fig. 2.** Back-scattered electron images of selected Khangar KHG tephra grains from (A) visible caldera deposit 154/90–352 (B) visible distal sample K7-T1-116 (C) ultra-distal, low concentration KHG cryptotephra deposit (1199.55–1199.40 m) from the NGRIP ice-core.





**Fig. 3.** (A) The stratigraphic position of the KHG tephra in NGRIP ice, plotted against the NGRIP  $\delta^{18}\text{O}$  profile (NGRIP members, 2004) and GICC05 age (Rasmussen et al., 2006, 2014; Vinther et al., 2006). The green bar indicates the age of the tephra in Greenland ice. (B) A prominent peak in the electrical conductivity measurement (ECM) coincides with the depth interval (green shading) in which the cryptotephra was found, and represents the likely chemostratigraphic signature of the KHG eruption. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 2**

Table showing major element values for each tephra deposit with associated standard deviations ( $2\sigma$ ). Major elements were obtained by EPMA analysis of individual grains and mean anhydrous (norm) values are expressed as % weight (%wt) of sample, together with average values of raw (hydrous) totals. The number of EPMA analyses (n) is given for each deposit. NGRIP 2016 EPMA analyses were performed at E-TAU, using a Cameca SX100 electron microprobe and all other EPMA analyses were performed at GEOMAR using JEOL JXA 8200 electron microprobe with analytical protocol described in Appendix A and by Ponomareva et al. (2017).

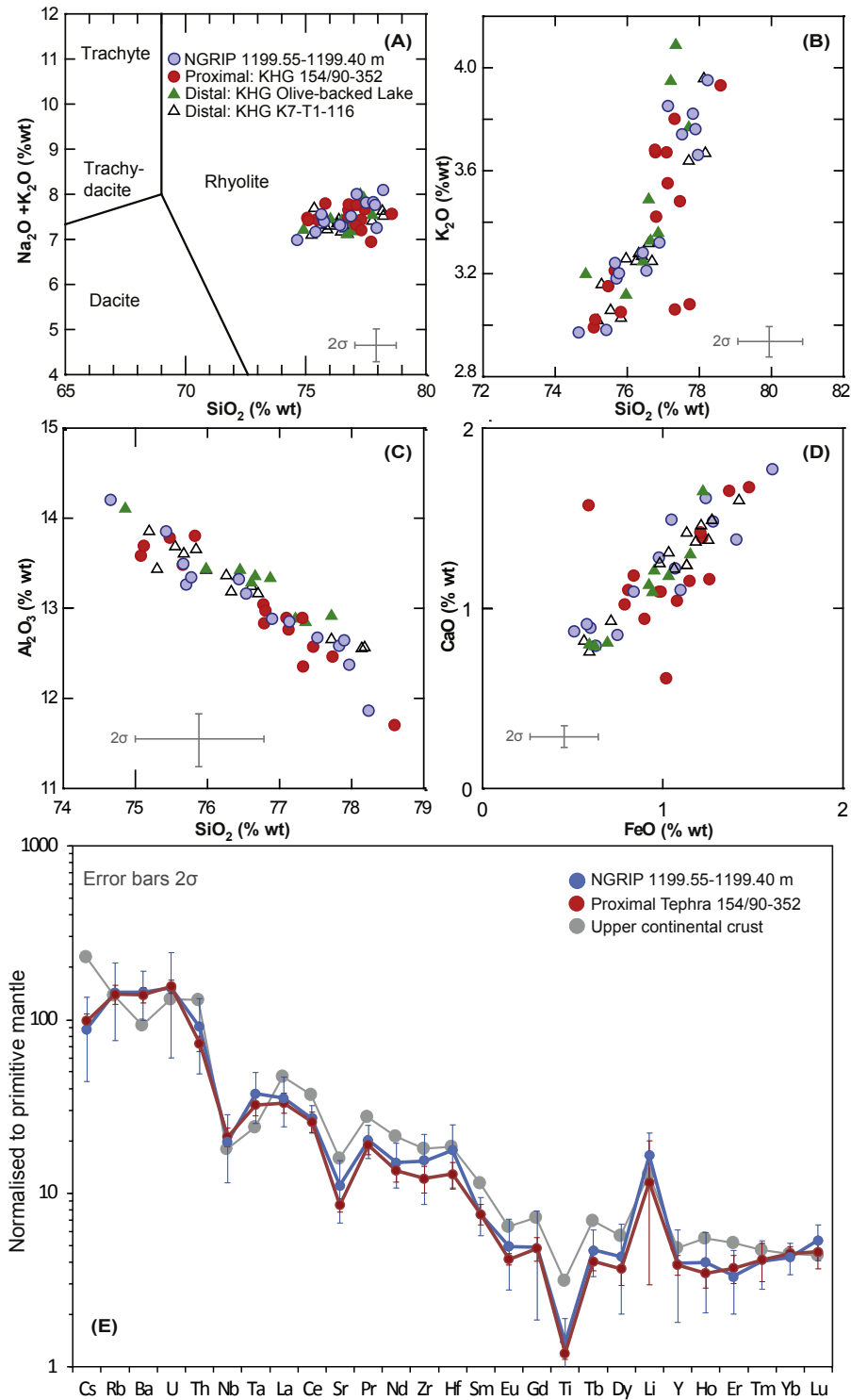
Major Elements	NGRIP 1199.55–1199.40 m (2017)		NGRIP 1199.55–1199.40 m (2016)		Khangar proximal 154/90–352 (2017)		Khangar proximal 154/90–352 (2011)		Khangar distal K7-T1–116 (2017)	
	Mean (n = 7)	$2\sigma$	Mean (n = 7)	$2\sigma$	Mean (n = 8)	$2\sigma$	Mean (n = 7)	$2\sigma$	Mean (n = 12)	$2\sigma$
SiO <sub>2</sub>	76.5	1.49	77.0	2.82	77.2	1.58	76.3	2.26	76.60	2.01
TiO <sub>2</sub>	0.18	0.13	0.17	0.16	0.22	0.05	0.24	0.08	0.21	0.12
Al <sub>2</sub> O <sub>3</sub>	13.2	0.58	12.9	1.66	12.8	1.13	13.3	1.01	13.26	0.89
FeO	1.02	0.56	0.93	0.81	0.92	0.37	1.19	0.43	1.02	0.54
MnO	0.05	0.06	0.06	0.04	0.04	0.04	0.04	0.06	0.05	0.07
MgO	0.23	0.18	0.23	0.20	0.16	0.09	0.26	0.12	0.24	0.18
CaO	1.23	0.52	1.16	0.76	1.08	0.50	1.35	0.51	1.23	0.52
Na <sub>2</sub> O	4.17	0.23	4.02	0.41	4.13	0.63	4.08	0.71	4.01	0.37
K <sub>2</sub> O	3.39	0.57	3.49	0.81	3.48	0.57	3.28	0.65	3.34	0.57
P <sub>2</sub> O <sub>5</sub>	0.03	0.06	0.03	0.04	0.02	0.04	0.02	0.03	0.03	0.05
<b>Total</b>	<b>96.9</b>	<b>0.44</b>	<b>97.7</b>	<b>0.77</b>	<b>94.6</b>	<b>0.44</b>	<b>97.1</b>	<b>0.59</b>	<b>96.74</b>	<b>1.81</b>

subparallel to that of the average upper continental crust (UCC) with values 2–3 times lower for most trace elements, except Rb, Ba, U, Nb, Ta, Li, Tm, Yb and Lu, which have similar concentrations to the UCC (Fig. 4e). Overall, the spectra indicate subduction-related provenance, evidenced by strong enrichment in Cs, Ba, Rb, U and Th relative to La. Distinctive features of these melts are, however, relatively high Nb and Ta contents and their less pronounced depletion relative to La in mantle normalised spectra, in comparison to UCC and typical arc-type magmas. These dual features testify these magmas as intermediate; between typical arc-type rhyolites and those formed in an intraplate setting, thus typical for magmas formed in the Sredinny Range of Kamchatka (e.g. Volynets, 1994). Such genetic source-related features are mostly preserved in the

left part of spectra, while the shape of the right part exhibits strong effects of magmatic phase-equilibria on the composition of these melts. Statistical analysis of 15 trace elements pairs between samples produces a  $D^2$  value of 6.064, below the  $D^2_{\text{critical}}$  value of 30.58 at the 99% confidence level, thus supporting the correlation (Table 3).

#### 4. Discussion and conclusions

Based on close ages and the strong resemblance of major and trace element compositions that indicate a cogenetic relationship between the glasses of NGRIP 1199.55–1199.40 m and KHG terrestrial deposits, we propose that the Greenland cryptotephra



**Fig. 4.** (A–D) Element–element biplots showing the geochemical relationship between NGRIP 1199.55–1199.40 m and KHG terrestrial samples. Geochemical data are normalised to 100% (anhydrous basis) and analyses with totals below 94 %wt were excluded. Error bars represent average 2 standard deviations ( $2\sigma$ ) of single microprobe points on the basis of long-term data on reference glasses at GEOMAR (Ponomareva et al., 2017); (E) Mantle-normalised trace element patterns of average glass compositions from NGRIP and KHG proximal sample 154/90-352, from the Khangar caldera. Upper continental crust is from Rudnick and Gao (2003) and primitive mantle is from McDonough and Sun (1995).

represents the ultra-distal ash fall deposit from the KHG eruption. The direct distance between NGRIP and Khangar is about 5600 km, although the pathway of ash transportation may have been extended under the influence of westerly winds (example in Fig. 1). Kamchatka is one of the world's most volcanically active areas and

two other Kamchatka tephra, both from Ksudach volcano (South Kamchatka) have been found in the North Atlantic region, in Holocene records: KS<sub>1</sub> in peatlands of Eastern Canada (Mackay et al., 2016) and KS<sub>2</sub> in a lake record from Svalbard (van der Bilt et al., 2017). These studies highlight the long-distance impact of

**Table 3**

This table presents similarity coefficients (SC) and statistical difference ( $D^2$ ) values for major elements (normalised to 100%), and  $D^2$  values for trace elements (T). Five major elements (with >1 %wt) were used for SC calculations, based on the method from Hunt et al. (1995), where values > 0.95 suggest products are from the same volcanic source.  $D^2$  is from Perkins et al. (1995, 1998) and seven major elements were used in the comparisons (with >0.01%wt). The value for testing the statistical distance values at the 99% confidence interval is 18.48 (7 degrees of freedom). For calculating trace element  $D^2$ , 15 elements were used (Pearce et al., 2008) and the value for testing  $D^2$  at the 99% confidence interval is 30.58 (15 degrees of freedom).

Major and Trace Element Comparison			
Sample Name	154/90-352	K7-T1-116	OBL
NGRIP 1199.55-1199.40 m	SC 0.982 $D^2$ 0.48 $D^2$ 6.064(T)	SC 0.973 $D^2$ 0.466	SC 0.971 $D^2$ 0.404

**Table 4**

Trace element data are expressed in ppm. Samples were analysed at the Institute of Geosciences at Christian-Albrecht University of Kiel, Germany using a Coherent Geolas ArF 193 nm Excimer laser ablation (LA) unit coupled to a Agilent 7500s (sample 154/90-352) or a Agilent 7900 QP-ICP-MS (NGRIP 1199.55-1199.40 m).

Trace Elements	NGRIP 1199.55-1199.40 m		Khangar proximal 154/90-352	
	Mean (n = 7)	2 $\sigma$	Mean (n = 8)	2 $\sigma$
Rb	86.1	40.7	83.7	10.7
Sr	220	86.4	170	15.0
Y	17.1	9.30	16.6	2.17
Zr	160	69.8	128	22.8
Nb	13.1	5.59	13.9	1.69
Cs	1.87	0.94	2.06	0.20
Ba	950	297	913	88.9
La	22.9	7.34	21.40	2.64
Ce	45.3	8.20	43.27	5.65
Pr	5.14	1.11	4.81	0.60
Nd	18.8	5.39	16.88	2.35
Sm	3.08	0.75	3.08	0.42
Eu	0.76	0.33	0.64	0.05
Gd	2.66	1.64	2.62	0.41
Tb	0.47	0.14	0.40	0.05
Dy	2.91	1.55	2.48	0.49
Ho	0.60	0.29	0.52	0.09
Er	1.46	0.58	1.62	0.30
Tm	0.26	0.08	0.26	0.06
Yb	1.88	0.38	1.99	0.18
Lu	0.36	0.08	0.31	0.06
Hf	5.00	2.01	3.65	0.62
Ta	1.38	0.45	1.19	0.16
Pb	—	—	10.21	1.91
Th	7.17	3.31	5.79	0.61
U	3.08	1.86	3.14	0.28

eruptions from Kamchatka, but do not permit the refinement of tephra ages. Here, the first identification of a Kamchatka tephra in a high-resolution Greenland ice-core elevates the significance of the KHG tephra as a hemispheric isochron, as the newly assigned GICC05 age of  $7950 \pm 50$  a b2k ( $7872 \pm 50$  a BP 1950) can be transferred to this key marker deposit.

This is the first discovery of KHG outside the Kamchatka Peninsula, which opens possibilities for tracing this deposit in other records, such as marine or terrestrial sediments of the Pacific and Arctic regions. By establishing this correlation, we were afforded an opportunity to examine the reliability of existing  $^{14}\text{C}$ -derived age estimates for the KHG eruption that are incorporated into age models for Kamchatka (e.g. Ponomareva et al., 2015). The accepted KHG age is 7620–7920 cal a BP (Braitseva et al., 1997; Bazanova and Pevzner, 2001) and we determine that these estimates are too young. Records that contain KHG can now improve and refine their chronologies through the use of the GICC05-derived age. Furthermore, in Greenland ice, the KHG layer falls  $189 \pm 3$  years after the end of the prominent 8.2 ka BP event, which may be linked to a cold period of glacial advance between 9 and 8 ka BP in Kamchatka,

evidenced in lacustrine (Dirksen et al., 2013; Brooks et al., 2015) and glacial till deposits (Barr and Solomina, 2015). KHG could be used to constrain the end of this cold event in Kamchatka, and explore climate evolution and synchronicity between the Pacific northwest and Greenland.

The identification of ultra-distal tephra highlights that eruptive volumes of explosive eruptions, based on terrestrial data from Kamchatka might be seriously underestimated. KHG was a catastrophic eruption and its signature in Greenland ice is manifested as both an ash deposit and as a prominent acid peak in the ECM chemostratigraphy. Although this event did not appear to have any cooling influence on air temperature, the potential exists to identify more Kamchatka-origin deposits in Greenland ice, such as the Kurile Lake caldera event ( $\sim 8.4$  cal ka BP with an eruptive volume of  $140\text{--}170 \text{ km}^3$ , Ponomareva et al., 2004) and investigate any lasting effects of volcanic forcing (e.g. Sigl et al., 2015) from the northwest Pacific region on the climate.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.quascirev.2017.11.036>.

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